Development of Novel Water-Gas-Shift Membrane Reactor

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Objectives

- Synthesize and characterize CO_2-selective membranes for the novel water-gas-shift (WGS) membrane reactor.
- Use the membrane data obtained in the mathematical model developed to show the feasibility of achieving H_2 enhancement via CO_2 removal and CO reduction to 10 ppm or lower and to elucidate the effects of system parameters on the reactor from the modeling study.
- Develop the membrane reactor for achieving H_2 enhancement and <10 ppm CO.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- L. Hydrogen Purification/Carbon Monoxide Cleanup

Approach

- Synthesize and characterize CO_2-selective membranes containing amino groups.
- Use the membrane data obtained in the modeling work to study membrane reactor performance and to guide/minimize experimental work.
- Incorporate the membrane synthesized in the reactor to demonstrate H_2 enhancement via CO_2 removal and CO reduction to 10 ppm or lower.

Accomplishments

- Synthesized membranes with high CO_2 permeabilities and high CO_2/H_2 and CO_2/CO selectivities.
- Elucidated the effects of system parameters including CO_2/H_2 selectivity on the membrane reactor for synthesis gases from autothermal reforming.
- Showed the feasibility of achieving H_2 enhancement via CO_2 removal, CO reduction to $\leq$10 ppm, and high H_2 recovery based on the modeling study using the membrane data obtained.
- Obtained <10 ppm CO in the H_2 product in initial WGS membrane reactor experiments using the synthesis gas feed with 1% CO.

Future Directions

- Continue to synthesize and characterize improved membranes for the reactor.
- Complete the proof-of-concept demonstration using the lab membrane reactor.
- Conduct the prototype membrane reactor demonstration for a fuel cell.

Introduction

A water-gas-shift (WGS) reactor for the conversion of carbon monoxide (CO) and water to hydrogen (H_2) and carbon dioxide (CO_2) is widely used in chemical and petroleum industries. The reactor is also critically needed for the conversion of fuels, including gasoline, diesel, methanol, ethanol, natural gas, and coal, to H_2 for fuel cells. Since the WGS reaction is reversible, it is not efficient, resulting in a high concentration of unconverted CO (~ 1%) in the H_2 product and a bulky, heavy reactor. This reaction can be enhanced significantly through a CO_2-selective membrane, which removes the reaction product, CO_2, to beat the reaction equilibrium and shift the reaction towards the product side. The CO_2-selective WGS membrane reactor has advantages including (1) a high-purity H_2 product is recovered at the high pressure (feed gas pressure) and (2) air can be used as the sweep gas to remove the permeate, CO_2, on the low-pressure side of the membrane to have a high driving force for the separation. These advantages are especially important for fuel cell vehicles. The first advantage eliminates the need for an unwanted compressor. With the second advantage, the high driving force created by the air sweep can result in low CO concentration and high H_2 purity and recovery.

Approach

We have synthesized novel CO_2-selective membranes by incorporating amino groups in polymer networks. The membranes synthesized were characterized in a gas permeation unit to determine their CO_2 permeabilities and CO_2/H_2 and CO_2/CO selectivities. We have used the selectivity and flux data obtained as the input to the mathematical model developed [1] to show the feasibility of achieving H_2 enhancement, CO reduction to ≤10 ppm, and high H_2 recovery; to study the effects of system parameters on the reactor; and to guide/minimize experimental work. In the model, the low-temperature WGS reaction kinetics for the commercial catalyst ($Cu/ZnO/Al_2O_3$) reported by Moe [2] and others [3] was used. In addition, we have incorporated the membrane synthesized in the laboratory WGS membrane reactor to show CO reduction to 10 ppm or lower in the H_2 product in initial reactor experiments using the synthesis gas feed with 1% CO.

Results

Synthesis and Characterization of Novel CO_2-Selective Membranes. Figure 1 shows the CO_2 permeability and CO_2/H_2 selectivity results as a function of temperature from 100°C to 180°C for the feed gas pressure of 2.1 atm and the sweep gas (air or nitrogen) of atmospheric pressure. As shown in this figure, the CO_2 permeability was about 4000 Barrers [1 Barrer = 10^{-10} cm^3(STP)-cm/cm^2-s-cmHg] or higher for the temperatures ranging from 100°C to 150°C. However, the permeability decreased to about 2000 Barrers as the temperature increased to 180°C. This was due to the reduction of water retention in the membrane as the temperature

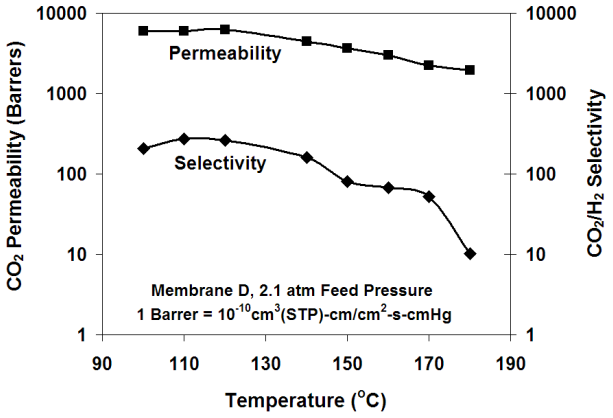

Figure 1. CO_2 Permeability and CO_2/H_2 Selectivity Results as a Function of Temperature

increased. Also shown in this figure, the CO_2/H_2 selectivity was about 100 or higher for the temperatures ranging from 100°C to 150°C. However, the selectivity decreased slightly as the temperature increased to 170°C. This was a result of the CO_2 permeability decrease due to the reduction of water retention in the membrane as described above. At 180°C, the selectivity decreased significantly to slightly greater than 10 due to the significant swelling of this membrane at this high temperature. Nonetheless, the selectivity of 10 is still good enough to give a high H_2 recovery of about 90%, which will be described in the following modeling work.

Figure 2 gives the CO_2 permeability results as a function of feed pressure from about 2 atm to about 4 atm at 150°C. As shown in this figure, the permeability did not change significantly with the feed pressure.

Figure 3 shows the CO_2/CO selectivity results as a function of temperature from 100°C to 160°C for the feed gas pressure of 2.1 atm. The CO_2/CO selectivity results were greater than 215, which is very good. However, the selectivity decreased as the temperature increased. This was a result of the CO_2 permeability decrease due to the reduction of water retention in the membrane as described above.

Modeling of Membrane Reactor Using Membrane Data Obtained. The CO_2/H_2 selectivity of 40 and the CO_2 permeability of 4000 Barrers were used in the modeling work. We have investigated the performance of the countercurrent membrane reactor for the synthesis gases from the autothermal reforming of gasoline with air. The three synthesis gases investigated at 3 atm contained CO at concentrations of 10%, 5%, and 1%. Figure 4 illustrates the profiles of the CO concentration in the H_2 product for a total reactor length of 61 cm for these three feed CO concentrations. As shown in this figure, a H_2 product with less than 10 ppm CO was obtained from each of these synthesis gases. In the membrane reactor, for each of these synthesis gases, the syngas flow with an inlet temperature of 140°C was countercurrent to the flow of hot air sweep with an inlet temperature of 140°C, the molar flow rate ratio of the air sweep to the syngas (γ) was 1.5, and

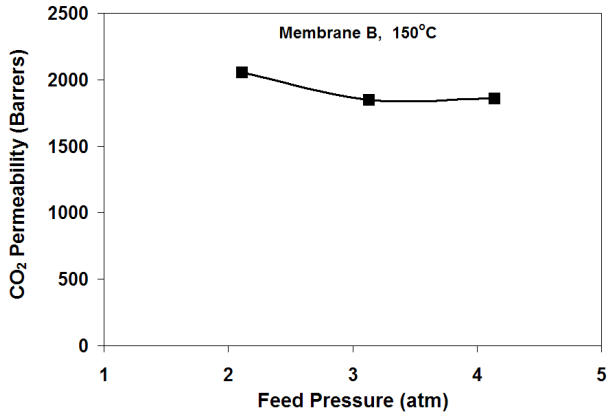

Figure 2. CO_2 Permeability Results as a Function of Feed Pressure at 150°C

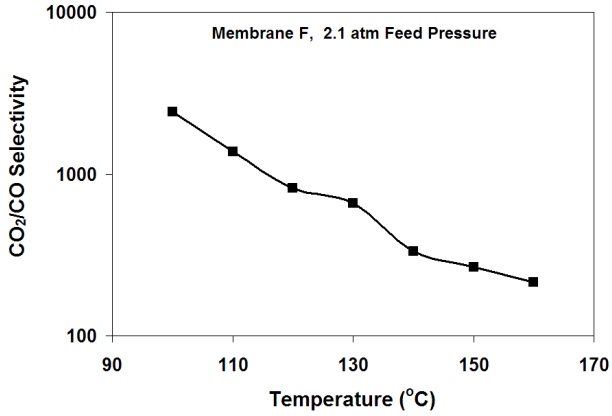

Figure 3. CO_2/CO Selectivity Results as a Function of Temperature

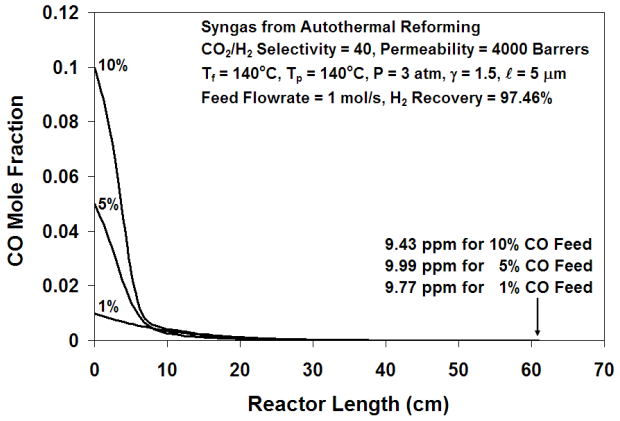

Figure 4. Profiles of Carbon Monoxide Mole Fractions in the Hydrogen Products along the Membrane Reactors for 10%, 5%, and 1% CO Feed Gases

the catalyst was the commercial Cu/ZnO supported on alumina.

For each of these synthesis gases, significant H_2 enhancement was achieved via CO_2 removal. For example, the H_2 concentration was increased from 41% in the inlet 1% CO feed gas to 48.5% in the outlet H_2 product on the wet basis (from 45.3% to 53.6% on the dry basis). Similar significant H_2 enhancement was also achieved for the 5% and 10% CO feed gases. In addition, a high H_2 recovery of greater than 97.4% was obtained for these synthesis gases, as indicated in Figure 4.

We have also investigated the effects of CO_2/H_2 selectivity on exit CO concentration and H_2 recovery for these synthesis gases through the modeling. For the CO_2/H_2 selectivity ranging from 10 to 80, the exit CO concentration of less than 10 ppm was achievable. A lower selectivity actually resulted in a slightly lower exit CO concentration as a lower selectivity (higher H_2 loss) enhanced the WGS reaction. However, the selectivity had a significant effect on H_2 recovery as depicted in Figure 5 for the 1% CO feed gas. A selectivity of 10 gave a H_2 recovery of about 90%, which is still quite good. As the selectivity increased, the H_2 recovery increased significantly. At the selectivity of 40, the H_2 recovery was greater than 97.4%, as mentioned earlier. For the selectivity of 60 or greater, the H_2 recovery was greater than 98.3%.

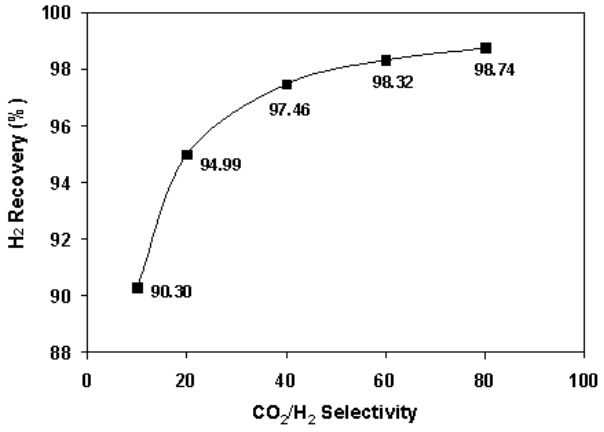

Figure 5. Effect of CO_2/H_2 Selectivity on H_2 Recovery for 1% CO Feed Gas

Initial Membrane Reactor Experiments. We began to incorporate the membrane synthesized in the laboratory WGS membrane reactor to conduct the proof-of-concept demonstration. In initial membrane reactor experiments, the commercial Cu/ZnO catalyst supported on alumina was placed on the top of the membrane, the operating temperature was 150°C, and the synthesis gas (from autothermal reforming) containing 1% CO was used. The rationale for using this synthesis gas was that it could be readily made from the commercial WGS reactor. In the initial membrane reactor experiments, a CO concentration of 10 ppm or lower in the H_2 product was obtained. This membrane reactor work is in progress.

Conclusions

We have synthesized membranes with high CO_2 permeabilities and high CO_2/H_2 and CO_2/CO selectivities. The membranes showed a high CO_2 permeability of about 4000 Barrers, a high CO_2/H_2 selectivity of greater than 40, and a high CO_2/CO selectivity of greater than 215 at 100 – 150°C. These membranes could be operated to about 180°C. Based on the modeling study using the membrane data obtained, we showed the feasibility of achieving H_2 enhancement via CO_2 removal, CO reduction to $\leq$10 ppm, and high H_2 recovery. In addition, we obtained <10 ppm CO in the H_2 product in initial WGS membrane reactor experiments using the synthesis gas feed with 1% CO.

References

1. W. S. W. Ho, "Development of Novel Water-Gas-Shift Membrane Reactor", Final Technical Report for the DOE Project Conducted at the University of Kentucky (September 2002).

2. J. M. Moe, "Design of Water-Gas-Shift Reactors", Chem. Eng. Progr., 58, 33 (1962).

3. R. L. Keiski, O. Desponds, Y. F. Chang, and G. A. Somorjai, "Kinetics of the Water-Gas-Shift Reaction over Several Alkane Activation and Water-Gas-Shift Catalysts", Applied Catalysis A: General, 101, 317-338 (1993).

FY 2003 Publications/Presentations

1. W. S. W. Ho, "Engineering Membranes for Environmental and Energy Applications", Invited Talk at the University of Illinois, Urbana, IL, September 24, 2002.

2. W. S. W. Ho, "Engineering Membranes for Environmental and Energy Applications", Invited Talk at Case Western Reserve University, Cleveland, OH, October 17, 2002.

3. L. El-Azzami and W. S. W. Ho, "Modeling of CO_2-Selective WGS Membrane Reactor for Fuel Cells", AIChE Annual Meeting, Indianapolis, IN, November 3 - 8, 2002.

4. W. S. W. Ho and Y. H. Tee, "CO_2-Selective Membranes Containing Mobile and Fixed Carriers", AIChE Annual Meeting, Indianapolis, IN, November 3 - 8, 2002.

5. W. S. W. Ho, "Engineering Membranes for Environmental and Energy Applications", Invited Talk at University of California, Riverside, CA, December 6, 2002.

6. W. S. W. Ho, "Development of Novel Water-Gas-Shift Membrane Reactor", Presentation to FreedomCAR Fuel Cell Tech Team, USCAR, Detroit, MI, 3/19/03.

Patent Pending

1. W.S. Winston Ho, "CO_2-Selective Membranes Containing Amino Groups", U. S. Patent Application Serial No. 10/145,297, filed on May 14, 2002.